

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TAKIMOTO HIROSHI

(22)Date of filing : 05.07.2000

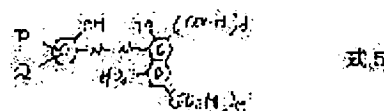
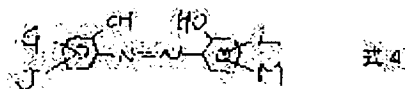
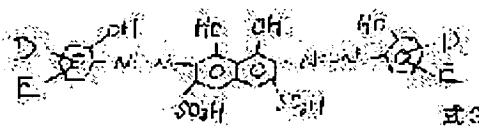
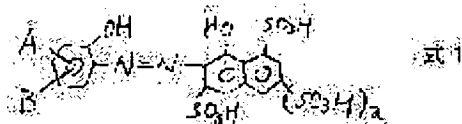
(72)Inventor : TAKIMOTO HIROSHI

## (54) RECORDING LIQUID

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a recording liquid capable of giving clear printed matters with a magenta color or a deep black color tone even when recorded on a plain paper a by ink jet recording, and not only excellent in print density, light resistance and weathering resistance (environmental polluting gas resistance), but also having good storage stability.

**SOLUTION:** The recording liquid comprises an aqueous medium and at least one coloring matter selected among metal complex coloring matters formed from a compound whose free acid form is represented by general formula (1), a compound whose free acid form is represented by general formula (2), a compound whose free acid form is represented by general formula (3), a compound whose free acid form is represented by general formula (4) or a compound whose free acid form is represented by general formula (5), and a salt of Cu, Co, Ni or Fe.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than  
the examiner's decision of rejection or  
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
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[Date of extinction of right]

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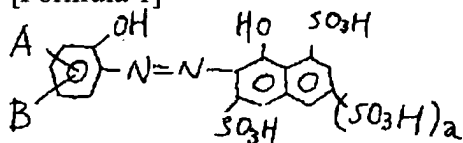
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## CLAIMS

## [Claim(s)]

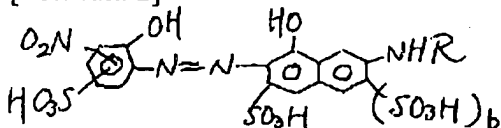
[Claim 1] Recording ink containing at least one sort of coloring matter chosen from the metal complex coloring matter formed from the salt of the compound shown by the compound shown by the compound shown by the compound shown by the compound or the following general formula (2) in which the form of a free acid is shown by the following general formula (1), or the following general formula (3), or the following general formula (4), or the following general formula (5), Cu, Co and nickel, or Fe.

## [Formula 1]



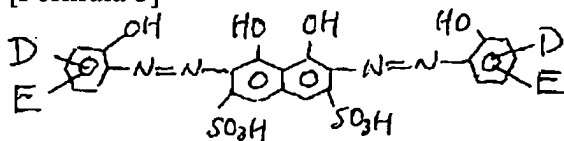
[-- as for the inside A of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, B expresses a hydrogen atom or a sulfonic acid group, and a expresses 0 or 1.]

## [Formula 2]



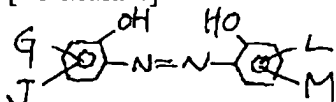
[-- as for the inside R of a formula, the phenyl group which may be permuted with the hydrogen atom, the carboxylic-acid radical, or the sulfonic acid group is expressed, and b expresses 0 or 1.]

## [Formula 3]



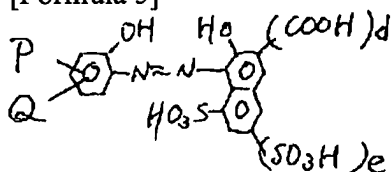
[-- as for the inside D of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, and E expresses a hydrogen atom or a sulfonic acid group.]

## [Formula 4]



[-- as for the inside G of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, J and M express a hydrogen atom or a sulfonic acid group according to an individual, respectively, and L expresses a hydrogen atom, an alkyl group, an alkoxy group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group.]

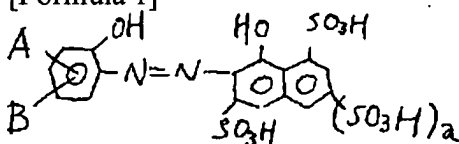
[Formula 5]



[-- as for the inside P of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, Q expresses a hydrogen atom or a sulfonic acid group, and d and e express 0 or 1 according to an individual, respectively.]

[Claim 2] Recording ink containing the metal complex coloring matter formed from the salt of the compound shown by the following general formula (1), Cu, Co, or nickel.

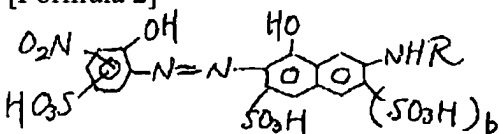
[Formula 1]



[-- as for the inside A of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, B expresses a hydrogen atom or a sulfonic acid group, and a expresses 0 or 1.]

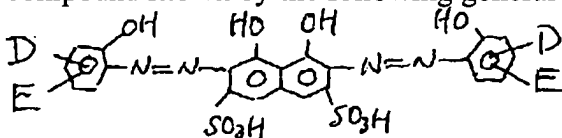
[Claim 3] Recording ink containing the metal complex coloring matter formed from the salt of the compound shown by the following general formula (2), Cu, Co and nickel, or Fe.

[Formula 2]



[-- as for the inside R of a formula, the phenyl group which may be permuted with the hydrogen atom, the carboxylic-acid radical, or the sulfonic acid group is expressed, and b expresses 0 or 1.]

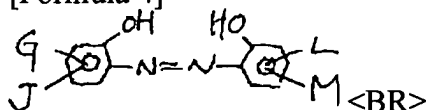
[Claim 4] Recording ink containing the metal complex coloring matter formed from the salt of the compound shown by the following general formula (3), Cu and nickel, or Co. [Formula 3]



[-- as for the inside D of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, and E expresses a hydrogen atom or a sulfonic acid group.]

[Claim 5] Recording ink containing the metal complex coloring matter formed from the salt of the compound shown by the following general formula (4), Cu, Co and nickel, or Fe.

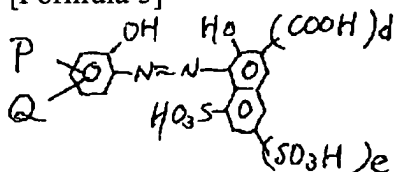
[Formula 4]



[-- as for the inside G of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, J and M express a hydrogen atom or a sulfonic acid group according to an individual, respectively, and L expresses a hydrogen atom, an alkyl group, an alkoxy group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group.]

[Claim 6] Recording ink containing the metal complex coloring matter formed from the salt of the compound shown by the following general formula (5), Cu, Co, or nickel.

[Formula 5]



[-- as for the inside P of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, Q expresses a hydrogen atom or a sulfonic acid group, and d and e express 0 or 1 according to an individual, respectively.]

[Translation done.]

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- 3.In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to recording ink. It is related with the recording ink which fitted the ink jet in detail.

[0002]

[Description of the Prior Art] The record approach by the ink jet method has come to be used extensively. As a coloring agent for recording ink used for this, water-soluble coloring matter or a pigment is used. Although a pigment is excellent in endurance, a color tone is blunt and anxiety is in distributed stability or regurgitation stability again. Although water-soluble coloring matter has a clear color tone, endurance division lightfastness and its weatherability are not enough. For this reason, water-soluble various coloring matter is proposed. Although it is said that azo metal complex coloring matter has high endurance, for example, the patent of a large number, such as JP,56-155,263,A, JP,57-30,773,A, JP,59-193,962,A, JP,63-46,260,A, and JP,3-97,772,A, is proposed, it has especially come to satisfy a demand of a commercial scene fully.

[0003]

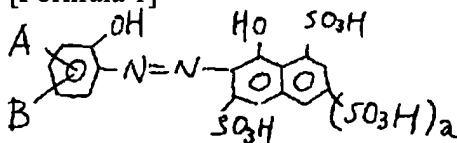
[Problem(s) to be Solved by the Invention] This invention aims at offering the recording ink for the image formation the concentration of a record image excelled [ image formation ] in weatherability and lightfastness with the color tone highly as an object for ink jet record.

[0004]

[Means for Solving the Problem] When the azo metal complex coloring matter of specific structure was used also in the azo metal complex coloring matter proposed until now, this invention person found out that it was satisfied with coincidence of the concentration, the color tone, and endurance of an image, and attained this invention. That is, the summary of this invention consists in the recording ink containing at least one sort of coloring matter chosen from the metal complex coloring matter formed from the salt of the compound shown by the compound shown by the compound shown by the compound shown by the following general formula (2) in which the form of a free acid is shown by the following general formula (1), or the following general formula (3), or the following general formula (4), or the following general formula (5), Cu, Co and nickel, or Fe.

[0005]

[Formula 1]

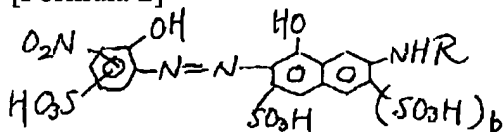


[-- as for the inside A of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, B expresses a hydrogen atom or a sulfonic acid group, and

a expresses 0 or 1.]

[0006]

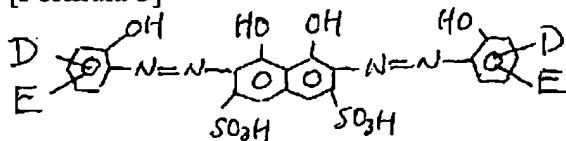
[Formula 2]



[-- as for the inside R of a formula, the phenyl group which may be permuted with the hydrogen atom, the carboxylic-acid radical, or the sulfonic acid group is expressed, and b expresses 0 or 1.]

[0007]

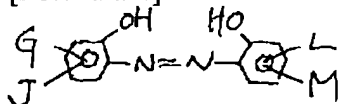
[Formula 3]



[-- as for the inside D of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, and E expresses a hydrogen atom or a sulfonic acid group.]

[0008]

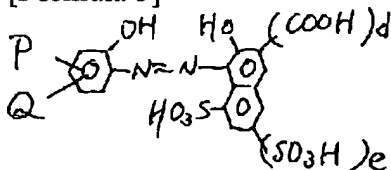
[Formula 4]



[-- as for the inside G of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, J and M express a hydrogen atom or a sulfonic acid group according to an individual, respectively, and L expresses a hydrogen atom, an alkyl group, an alkoxy group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group.]

[0009]

[Formula 5]



[-- as for the inside P of a formula, a hydrogen atom, a chlorine atom, a bromine atom, an alkyl group, a sulfonamide radical, a nitro group, the acylamino radical, a triazinylamino radical, a carboxylic-acid radical, or a sulfonic acid group is expressed, Q expresses a hydrogen atom or a sulfonic acid group, and d and e express 0 or 1 according to an individual, respectively.]

[0010]

[Embodiment of the Invention] This invention is explained to a detail below. The coloring matter used by this invention is an object chosen from the coloring matter shown by the coloring matter shown by the coloring matter shown by the coloring matter in which the form of a free acid is shown by said general formula (1), the coloring matter shown by said general formula (2), and said general formula (3), and said general formula (4), and said general formula (5).

[0011] In said general formula (1), a triazinylamino radical like a hydrogen atom, a chlorine atom, a bromine atom or a methyl group, an alkyl group like an ethyl group, a sulfonamide radical, a nitro group or an acetilamino radical, an acylamino radical like a benzoylamino radical, or a 4-friend no 6-hydroxy triazinylamino radical as a radical shown by A, a carboxylic-acid radical, or a sulfonic acid group is raised.

[0012] In said general formula (1), a hydrogen atom or a sulfonic acid group is raised as a radical shown by B.

[0013] In said general formula (2), as for R, a hydrogen atom, a phenyl group or a carboxyphenyl radical, and a sulfoxy phenyl group are raised.

[0014] In said general formula (3), a triazinylamino radical like a hydrogen atom, a chlorine atom, a bromine atom, a methyl group, an alkyl group like an ethyl group, a sulfonamide radical, a nitro group or an acetilamino radical, an acylamino radical like a benzoylamino radical, or a 4-friend no 6-hydroxy triazinylamino radical as a radical shown by D, a carboxylic-acid radical, or a sulfonic acid group is raised.

[0015] In said general formula (3), a hydrogen atom or a sulfonic acid group is raised as a radical shown by E.

[0016] A triazinylamino radical like a hydrogen atom, a chlorine atom, a bromine atom, a methyl group, an alkyl group like an ethyl group, a sulfonamide radical, a nitro group or an acetilamino radical, an acylamino radical like a benzoylamino radical, or a 4-friend no 6-hydroxy triazinylamino radical as a radical shown by G in said general formula (4), a carboxylic-acid radical, or a sulfonic acid group is raised.

[0017] In said general formula (4), a hydrogen atom or a sulfonic acid group is raised as a radical shown by J and M.

[0018] A triazinylamino radical like a hydrogen atom or a methyl group, an alkyl group like an ethyl group, a sulfonamide radical or an acetilamino radical, an acylamino radical like a benzoylamino radical, or a 4-friend no 6-hydroxy triazinylamino radical as a radical shown by L in said general formula (4), a carboxylic-acid radical, or a sulfonic acid group is raised.

[0019] A triazinylamino radical like a hydrogen atom, a chlorine atom, a bromine atom, a methyl group, an alkyl group like an ethyl group, a sulfonamide radical, a nitro group or an acetilamino radical, an acylamino radical like a benzoylamino radical, or a 4-friend no 6-hydroxy triazinylamino radical as a radical shown by P in said general formula (5), a carboxylic-acid radical, or a sulfonic acid group is raised.

[0020] In said general formula (5), a hydrogen atom or a sulfonic acid group is raised as a radical shown by Q.

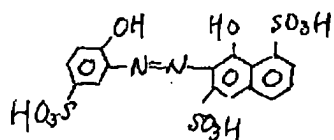
[0021] Although the free-acid mold showed the coloring matter used by this invention by said general formula, the salt of the ammonium which may be permuted in actual use by the salt of alkali metal or alkyl group like [ it is desirable that it is a salt type and ] Li, Na, and K as a salt type example, and the hydroxyalkyl radical, or the salt of an organic amine is raised. [0022] The example of the coloring matter used by this invention is described below. The complex-ized metal is described into () beside a coloring matter number.

[0023]

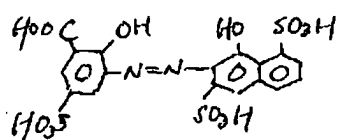
[Formula 6]



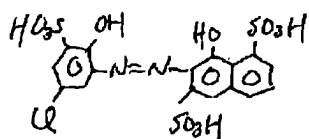
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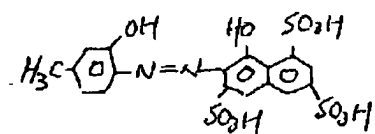
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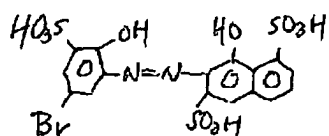
(1)-2 (Ni)



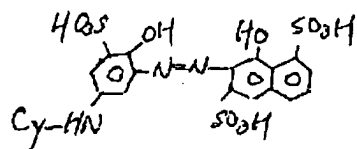
(1)-7 (Cu)



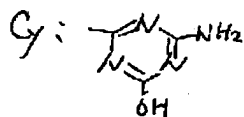
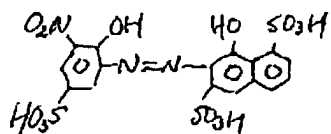
(1)-3 (Cu)



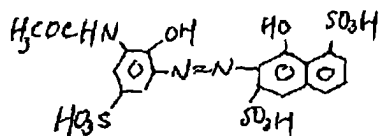
(1)-8 (Co)



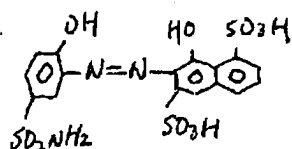
(1)-4 (Co)



(1)-5 (Cu)



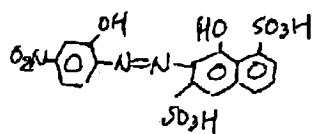
(1)-9 (Ni)



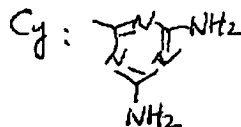
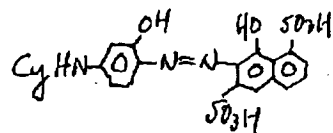
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[Formula 7]

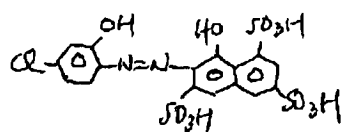
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(1)-11 (Cu)



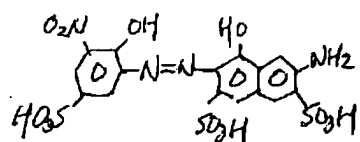
(1)-12 (Ni)



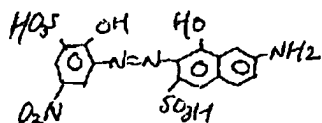
[0025]

[Formula 8]

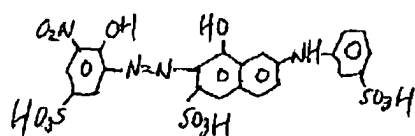
(2)-1 (Fe)



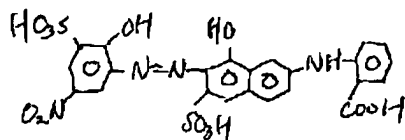
(2)-6 (Co)



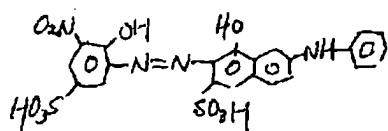
(2)-2 (Co)



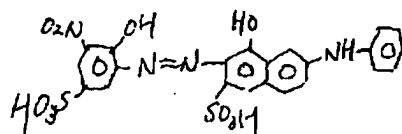
(2)-3 (Cu)



(2)-4 (Ni)



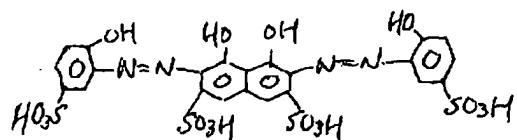
(2)-5 (Fe)



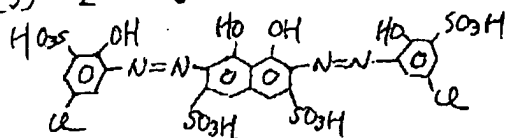
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[Formula 9]

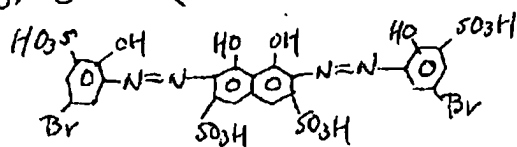
(3)-1. (Na)



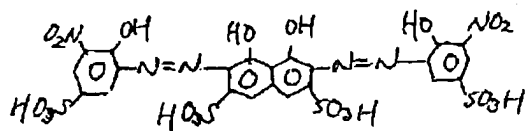
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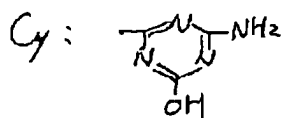
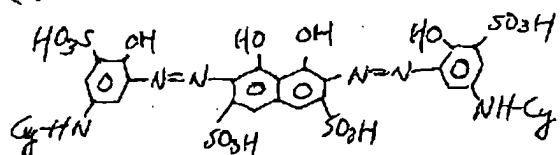
(3)-3 (Fe)



(3)-4 (Co)



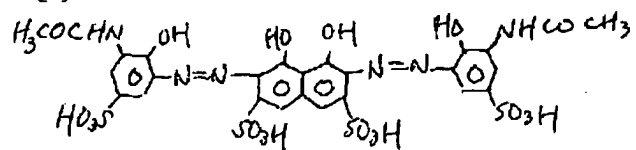
(3)-5 (Fe)



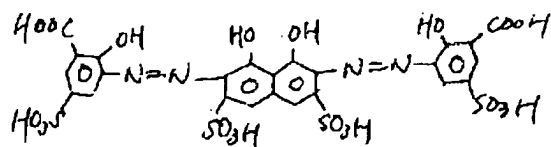
[0027]

[Formula 10]

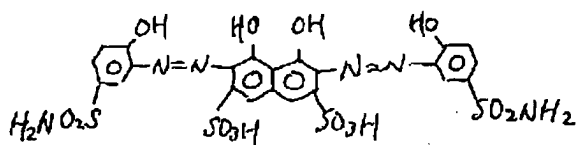
(3)-6 (Co)



(3)-7 (Na)



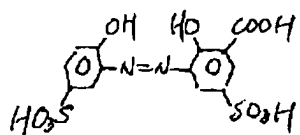
(3)-8 (Fe)



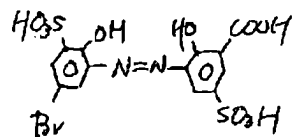
[0028]

[Formula 11]

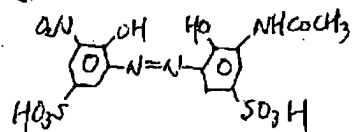
(4)-1 (Fe)



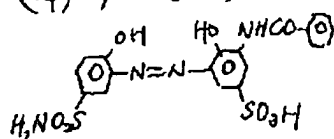
(4)-6 (Co)



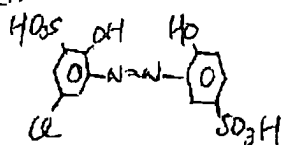
(4)-2 (Co)



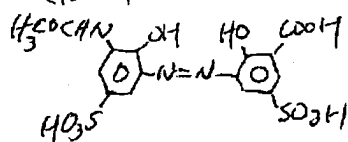
(4)-7 (Cu)



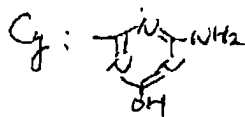
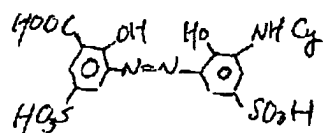
(4)-3 (Cu)



(4)-4 (Ni)



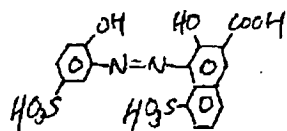
(4)-5 (Fe)



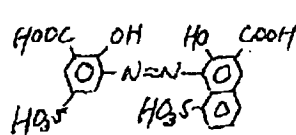
[0029]

[Formula 12]

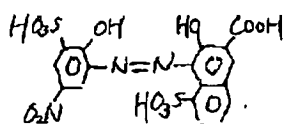
(5)-1 (Cu)



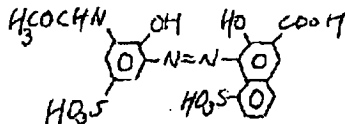
(5)-6 (Fe)



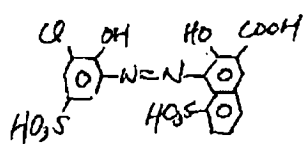
(5)-2 (Co)



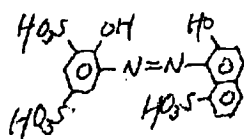
(5)-7 (Cu)



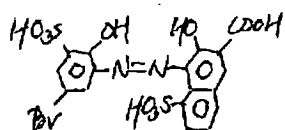
(5)-3 (Ni)



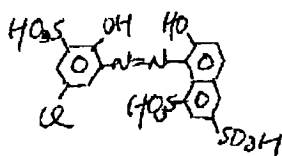
(5)-8 (Co)



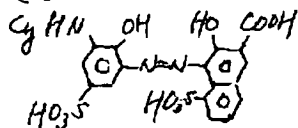
(5)-4 (Cu)



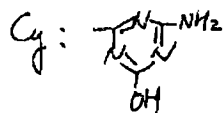
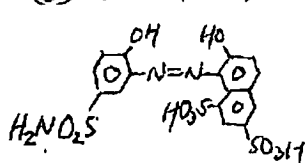
(5)-9 (Fe)



(5)-5 (Fe)



(5)-10 (Ni)



[0030] The above (1) The coloring matter shown by -1 can be manufactured at the following processes. After diazotizing 2-friend no phenol 4-sulfonic acid according to a conventional method (for example, \*\*\*\*\* publication written by new color chemistry Yutaka Hosoda 412 pages description of 14 to 19 lines) and carrying out coupling to the Epsilon acid, the coloring matter of copper-containing \*\*\*\*\* (1)-1 can be obtained using a copper sulfate. (2) It can obtain similarly about the coloring matter of - (5).

[0031] As a content of the coloring matter of said general formula in recording ink (1), (2), (3), (4), or (5), 0.5 - 8 % of the weight is desirable to all recording ink weight.

[0032] As an aqosity medium used for the recording ink of this invention, water and a water-soluble organic solvent are used, and ethylene glycol, a diethylene glycol, a polyethylene glycol, a glycerol, N-methyl pyrrolidone, the diethylene-glycol monobutyl ether, isopropanol, etc. are raised as a water-soluble organic solvent.

[0033] These water-soluble organic solvents are usually used 50% of the weight from one into recording

ink. On the other hand, water is used 95% from 45 into recording ink.

[0034] In the recording ink of this invention, quick-drying [ after printing ] and printing grace can be further improved by making 0.5 - 5% of the weight of a urea, 0.001 to 0.5% of the weight of a surfactant, etc. contain.

[0035]

[Example] Although an example explains this invention to a detail further below, this invention is not the object limited to these examples, unless the summary is exceeded. In addition, the section is taken as the object showing the semantics of the weight section.

[0036] Water was added to the [example 1] ethylene glycol 15 section, the isopropanol 3 section, and said coloring matter 3 section of general formula (1)-1, the lithium-hydroxide water solution adjusted pH to 9, and total weight was made into the 100 sections. After having fully agitated this constituent, dissolving and carrying out pressure filtration with a Teflon (trademark) filter with an aperture of 1 micrometer, degassing processing was carried out by the vacuum pump and the supersonic wave, and recording ink was adjusted.

[0037] Using the obtained recording ink, the ink jet printer (trade name JetWind500C, Fuji Xerox product) was used, ink jet record was performed in the electrophotography form, and the magenta color printing object of a clear color tone was obtained. Furthermore, the result of having evaluated by the approach of (a), (b), (c), and (d) is shown.

[0038] (a) Lightfastness of a record image : although the record image was turned inside the south windowpane, and the printing side was turned to the glass side and attached for two weeks, change in color of a record image was small.

[0039] (b) Weatherability of a record image : although the traffic of a vehicle put up the record image for the bottom of the guard upon whom neither rain nor direct rays shines mostly for one month, change in color of a record image was small.

[0040] (c) The water resisting property of a record image : although the record image was immersed for 5 minutes into tap water, the blot of a record image was small.

[0041] (d) Preservation stability of recording ink : recording ink was sealed to the carboy and saved for three months under the room temperature. The big and rough aggregate was not accepted as a result of visual observation.

[0042] Water was added to the [example 2] glycerol 5 section, the diethylene-glycol 5 section, the N-methyl pyrrolidone 5 section, and the coloring matter 5 section of aforementioned (2)-1, after caustic soda adjusted pH to 9, the whole quantity was made into the 100 sections, and recording ink was adjusted like the example 1. As a result of printing like an example 1 using this recording ink, the black printing object of a redness color tone was obtained. Evaluation by (a) of an example 1, (b), (c), and (d) was performed to this printing object. Consequently, each obtained the good result like the example 1.

[0043] The [example 3] ethylene glycol 5 section, the polyethylene-glycol (#400) 5 section, the diethylene-glycol monobutyl ether 1 section, said coloring matter (3)-1 Water was added to the five sections, aqueous ammonia adjusted pH to 10, the whole quantity was made into the 100 sections and recording ink was adjusted like the example 1. Using this recording ink, as a result of printing like an example 1, the printing object of a clear magenta color was obtained. Evaluation by (a) - (d) of an example 1 was performed to this printing object. consequently, it was alike like the example 1 and all obtained the good result.

[0044] To a change of the coloring matter of (1)-1 used in the [examples 4-43] example 1  
Aforementioned (1)2- (1) Except having used the coloring matter of -12, (2)-2-(2)-6, (3)-2-(3)-8, (4)-1-(4)-7, and (5)-1-(5)-10, it printed by having adjusted recording ink by the approach of an example 1, and the printing object was evaluated. Consequently, all as well as an example 1 obtained the good result.

[0045]

[Effect of the Invention] Even when the recording ink of this invention is used as an object for ink jet record and it records on a regular paper, the printing object of a clear magenta system or a black system is obtained, and it excels in printing concentration, lightfastness, and weatherability (environmental gas) nature, and also it excels in the preservation stability as recording ink.



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[Translation done.]